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Reduction of PbS and Sb₂S₃ with elemental Fe and Mg in dusty plasma environment created during electrical discharge assisted mechanical milling (EDAMM)

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Abstract

The newly developed synthesis technique of electrical discharge assisted mechanical milling (EDAMM) is used to reduce Pb and Sb sulfides using Fe and Mg as reduction agents. It is demonstrated that both Fe and Mg can successfully be used to fully reduce PbS and Sb_2S_3 in only 5 min using EDAMM. This is the fastest sulfide reduction technique so far developed, and has the added advantage of not requiring external heating of the reactants during processing. The reaction products are a solid mixture of larger crystal sizes than would be achieved through conventional milling.

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1. Introduction

In typical pyrometallurgical processes that are employed to obtain metals from ores (such as oxides or sulfides), the solid raw material is transformed to the product by a liquid and/or gas phase reaction. These processes require high reaction temperatures and pressures. The final products then require an additional processing step to separate the desired metal product from any by-products, remaining starting materials and/or from the solvent. Generally, the final product is solid again [1].

The preparation of metals and alloys by reduction of their salts can be expressed in general by the equation

$$M_1 X + M_2 \rightarrow M_1 + M_2 X \tag{1}$$

where M_1 is the reduced metal, M_2 is reducing metal and X anions as Cl^{-1}, O^{-2} or S^{-2} . The reducing metal must have a strong affinity for the compounds to be reduced. This method is characterized by the fact that the reducing metal is converted to

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0925-8388/\$ – see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2007.12.032 a solid or a liquid product and not to a gas as in other reduction processes, e.g., reduction by carbon or hydrogen. In general, such processes are called metallothermic [1].

Metal sulfides can be reduced by high temperature reaction with reducing metals such as Al, Ca, Mg, Na and Si (as FeSi). The most common reduction agent is scrap iron, because of its low cost. Balaz et al. [2–4] systematically studied the application of Fe as a mechanochemical reducing agent for copper (Cu₂S), lead (PbS), and antimony (Sb₂S₃). The reduction reactions resulted in the synthesis of nanocrystalline Cu, Pb and Sb in the range of 12–18 nm. During the milling process, these reaction products formed nanocomposites of Cu/FeS, Pb/FeS and Sb/FeS, and these are of interest as prospective materials for precursors of catalysts for heterogeneous chemical reactions.

Apart from using Fe, there are also several examples of Mg being used as a reducing agent. Mechanical milling with Mg utilizes the high affinity of magnesium metal for oxygen to enable the reduction of oxidic compounds. Nasu et al. [5] milled hematite with Mg powder, and observed the formation of α -Fe together with MgO as the product phases. El-Eskandarany et al. [6] studied the kinetics and mechanism of the mechanochemical reaction between Fe₂O₃ and Mg and confirmed the single step



Fig. 1. Schematic of electrical discharge assisted mechanical milling (EDAMM).

reaction procedure with α -Fe and MgO as the only reaction products. In that case the reaction proceeds with one-dimensional growth and is diffusion controlled [7]. Welham [8] has also used Mg metal for the reduction of ilmenite FeTiO₃ by high-energy mechanical milling. Matteazzi and Le Caer [9] were the first to study the solid-state reduction of metal sulfides with pure metals by applying high-energy mechanical milling. It was shown that the reduction of metal sulfides with a suitable reducing metal is feasible using room temperature vibratory milling. Metals, alloys, intermetallic compounds and nanocomposites were synthesized, and had crystallite sizes in the range 10–30 nm [9].

These examples of mechanical milling being used to reduce sulfides and oxides to metal using a reducing agent have proved the ability of this technique to synthesize many metals from their compounds. Recently, a new high-energy milling technique has been developed [10]. Electric discharge assisted ball milling (EDAMM) is a synthesis technique based on mechanical milling, but includes an additional repeated electrical discharge and/or plasma that is formed around the reacting particles during milling. This new technique has been shown to increase the rate of reaction compared to conventional milling, and is also known to initiate reactions that are not possible using conventional mechanical milling. This increased reactivity results primarily from formation of complex plasma generated by electric discharge. High-energy mechanical milling offers great potential for the rapid synthesis of metals and compounds [11]. During mechanical milling, the diffusion rates of the reacting powders are substantially increased by the introduction of a large number of solid defects, and also by a reduction in the crystallite size of the reactants. This technique has been applied to the synthesis of a wide variety of nanocrystalline compounds, for example, see refs. [12,13].

The following paper describes the use of Fe and Mg in the reduction of PbS and Sb_2S_3 using EDAMM. It is shown that EDAMM is a rapid and highly energy efficient synthesis



Fig. 2. XRD patterns of (a) PbS + Fe starting powder after pre-mixing and (b) $FeS_2 + Pb$ powder produced by EDAMM.



Fig. 3. XRD patterns of (a) PbS + Mg starting powder after pre-mixing and (b) MgS + Pb powder produced by EDAMM.



Fig. 4. XRD patterns of (a) Sb_2S_3 + Fe starting powder after pre-mixing and (b) FeS + Sb + Sb_2O_3 powder produced by EDAMM.

technique. Moreover, this is the first use of Mg metal for the reduction of metal s ever reported.

2. Experimental method

PbS and Sb_2S_3 powders were mixed with stoichiometric portions of both Fe and Mg to obtain complete reduction of PbS/Sb₂S₃ and produce MgS or FeS. These starting powder mixtures were first mechanically pre-mixed in a conventional ball mill for 1 h under a high purity argon atmosphere. This premixture was then subjected to 5 min of electric discharge assisted ball milling.

Electric discharge assisted ball milling was performed in a modified vibrational laboratory rod mill. This technique produces a milling mode that combines



Fig. 5. XRD patterns of (a) $Sb_2S_3 + Mg$ starting powder after pre-mixing and (b) Sb + MgS powder produced by EDAMM.



Fig. 6. Scanning electron micrographs of (a) PbS + Fe starting powder after premixing and (b) $FeS_2 + Pb$ powder produced by EDAMM. Scale bars = 20 μ m.

repeated impact of a hardened curved rod end on powder particles, under electrical conditions of pulsed arc discharges (Fig. 1). The electric discharges were generated during milling in the gaps between the vibrating mill base, the powder particles and a loosely suspended conducting plunger. The power supply used in this study generated radio frequency impulses within the kV/mA range. During vibration, small gaps between the stainless steel rod and the chamber wall resulted in an electric discharge (Fig. 1) and formation of dust cloud between electrodes. Electric discharge induces high chemical reactivity in between the powder particles that are suspended between electrodes (the plunger and the chamber). The mechanism of chemical reactions between powder particles surfaces induced by electric discharge is complex and poorly understood. However, the most important factors that contribute to enhanced reactivity are the formation of plasma environment between powder particles, formation and acceleration of ions and free radicals under fast moving stream of electrons, and bombardment (implantation and deep penetration) of ions and free radicals on powder particle surfaces. This process also causes the formation of channels on the particles' surface. This results in an increase in the total surface area and therefore an increase in the rate of diffusional processes. In addition, the powder particles are constantly being mixed and fractured by the vibrating electrode. This process, which is analogous to conventional mechanical milling, also increases the surface area and reactivity of the powder mixture.

EDAMM was carried in a high purity Ar flowing at a rate of 0.3 m^3 /min. In all experiments, a milling time of 10 min was used. X-ray diffraction (XRD) analysis of the as-milled powders was performed using a Phillips PW1730 diffractometer with a graphite monochromator and Cu K α radiation. Phase identification was carried out using the International Centre for Diffraction Data (JCPDS-ICDD 2000) powder diffraction files (PDF). The morphology of the powders was observed by a Leica 440 Stereoscan scanning electron microscope (SEM). This SEM is equipped with an Oxford Instruments ISIS energy dispersive spectroscopy



Fig. 7. Scanning electron micrographs of (a) PbS + Mg starting powder after premixing and (b) MgS + Pb powder produced by EDAMM. Scale bars = $20 \mu m$.

(EDS) system which was used to examine the composition of the powders.

3. Experimental results

3.1. X-ray diffraction

An X-ray diffraction spectrum of the pre-mixed PbS and Fe powders is shown in Fig. 2a. It can be seen that after 1 h of conventional ball milling there has been no reaction between the PbS and the Fe. However, after 5 min of EDAMM, strong diffraction peaks are evident for the FeS₂ and Pb phases (Fig. 2b). There is complete reaction from PbS + Fe to $FeS_2 + Pb$, since no diffraction peaks from the reactant powders are evident after EDAMM (Fig. 2b). A very similar result is obtained from the mixture of PbS and Mg. Pre-mixing for 1 h does not show any reaction between the PbS and Mg (Fig. 3a), but after 5 min EDAMM, XRD shows complete reaction to Pb + MgS (Fig. 3b).

The reaction between Sb_2S_3 and Fe during EDAMM was slightly more complicated. XRD confirmed that the pre-mixing of Sb_2S_3 and Fe did not induce any chemical reaction (Fig. 4a). However, after EDAMM, XRD revealed that although elemental Sb was produced, the other reaction products were a mixture of FeS and Sb_2O_3 (Fig. 4b). The diffraction peaks from the Sb_2O_3 were not high in intensity, and this suggests that there was only



Fig. 8. Scanning electron micrographs of (a) $Sb_2S_3 + Fe$ starting powder after pre-mixing and (b) $FeS + Sb + Sb_2O_3$ powder produced by EDAMM. Scale bars = (a) 10 μ m and (b) 20 μ m.

a small amount produced during EDAMM. The pre-mixing and EDAMM were carried out in an inert atmosphere, so it is likely that the small amount of oxygen present in the reaction products was introduced into the system from the Fe powder.

The reaction between Sb_2S_3 and Mg did not produce any oxides. The pre-mixture, which remained unreacted after conventional milling (Fig. 5a) formed Sb and MgS after EDAMM (Fig. 5b).

3.2. Scanning electron microscopy

After conventional ball milling, the PbS and Fe mixture consisted of small particles $\sim 10 \,\mu\text{m}$ in diameter. After EDAMM, the reacted powder formed large agglomerates that were 200–300 μ m in diameter (Fig. 6).

The mixed PbS and Mg powders formed large unreacted agglomerates during conventional ball milling (Fig. 7a). Following EDAMM, the MgS + Pb mixture formed relatively small agglomerates of around 25 μ m in diameter (Fig. 7b).

The conventionally milled Sb_2S_3 and Fe powders did not agglomerate, but remained as individual particles in the mixture. After EDAMM, the products formed larger particles of $\sim 30 \,\mu m$ in diameter. These particles typically displayed smooth outer surfaces indicative of localized melting during EDAMM (Fig. 8). A similar behaviour was displayed by the $\mathrm{Sb}_2\mathrm{S}_3$ and Mg powders (Fig. 9

).

The distribution of the reaction products within individual powder particles was further examined using compositional mapping in the SEM, and an example is shown in Fig. 10. The backscattered electron (BSE) image is shown on the top left. The size and morphology of the constituents in the agglomerate are visible. The compositional mapping confirms that the lighter regions are Sb, and that these Sb regions are depleted in S. The Sb regions are surrounded by MgS. X-ray mapping for the other samples examined in this study are shown in Figs. 11–13.

4. Discussion

The XRD results shown here in Figs. 2 and 3 show that PbS and Sb_2S_3 can successfully be reduced by EDAMM using either Fe or Mg as the reducing agent. Using conventional pyrometallurgical techniques, the reduction of these sulfides by Mg is not possible. However, it has been shown here that complete reduction can be achieved in 5 min using EDAMM. In fact, Mg appears to be a better reducing agent than Fe – the samples of Sb_2S_3 milled with Fe formed some oxides as a result of contamination from the Fe powder. Oxide contamination was not detected when Mg was used as the reducing agent (Fig. 5).

There has been previous research into the reduction of metal sulfides by mechanical milling. For example, Balaz et al. [3] have reduced PbS and CuS by conventional milling using Fe as the reducing agent. In that case, the reduction reactions required up to 20 min to reach the maximum reaction of 90%. Mechanical



Fig. 9. Scanning electron micrographs of (a) Sb_2S_3+Mg starting powder after pre-mixing and (b) Sb+MgS powder produced by EDAMM. Scale bars = 20 μ m.



Fig. 10. Elemental mapping of a particle of Sb+MgS after EDAMM. The backscattered electron (BSE) image is shown, along with the composition maps for Mg, S and Sb as indicated.



Fig. 11. Elemental mapping of a particle of $Pb + FeS_2$ after EDAMM. The backscattered electron (BSE) image is shown, along with the composition maps for Fe, S and Pb as indicated.



Fig. 12. Elemental mapping of a particle of Pb+MgS after EDAMM. The backscattered electron (BSE) image is shown, along with the composition maps for Mg, S and as indicated.



Fig. 13. Elemental mapping of a particle of Sb + FeS after EDAMM. The backscattered electron (BSE) image is shown, along with the composition maps for Fe, S and Sb as indicated.

milling reduces the size of the reactant particles to around 15 nm. This dramatic increase in the surface area of the reacting powders is the reason that mechanical milling is successful in driving the reduction reaction. EDAMM combines the increase in surface area afforded by mechanical milling, with rapid chemical reactions generated by plasma around the reactants.

It might be expected that localized heating in our device generates high temperature plasma, and that the precursor powders are vaporized and then rapidly quenched throughout the con-



Fig. 14. Schematic representation of "dusty plasma" developed during EDAMM.

densation process. However, SEM results suggest a different reaction mechanism. Only in Fig. 8b can melted particles can be identified, all other SEM micrographs showed agglomerates of small particles that did not exhibit melting. Although, some powder particles can be melted during EDAMM, the purpose of using the impulse mode is to prevent massive melting, and to keep the precursor powders in solid form from the beginning up to the end of the process. This leads to the formation of what we have termed a "dusty cloud" between the electrodes. The dust particles become suspended in the plasma in a region between the plunger and the mill base. The general aim is to create dusty plasma environment which, we believe, will be more effective in generation of reduction reactions than thermal plasma.

In the milling device used in this study, the plunger and the base vibrate independently. The purpose of vibrating the base is to ensure the powder does not lie stationary on the plunger base. If the base was not vibrating, the powder would stay at the bottom of the reaction chamber and would not be suspended between the base and the plunger. In that case the powder laying on the base is subjected to both mixing (or milling) by the plunger and discharges in the gaps between the plunger and the stationary powder. We found that in this condition only about 10% reaction can be achieved after 5 min of EDAMM. However, if both the plunger and the base vibrate, full reaction is achieved within 5 min. This means that the effectiveness of EDAMM is strongly dependent on powder movement during milling. This represents a significant improvement in our understanding of the parameters that promote high reaction rates during EDAMM.

Although, the reactions occurring during EDAMM are poorly understood, we may say that the first step in plasma processing is the production of plasma by ionization. Primary ions of a carrier gas (Argon) are produced, which then transfer excitation and ionization to powder particle surfaces, producing ions and radicals - the reactant precursors. The plasma flow of gas ions, free radicals and reactant ions bombard the powder surfaces with high energy causing ion implantation. The interaction between the particle surface and the arriving radicals leads to the nucleation and growth of new phases by deep penetration of ions and subsequent diffusion. A possible mechanism is shown in Fig. 14. Additionally, under the flux of electrons and ions, a thin surface layer on the outside of some particles may be melted. These can form agglomerates under the influence of electrostatic forces, and these agglomerates are seen in the SEM micrographs (e.g., Fig. 6). The localized heating also results in the crystallite size of the reaction products being much larger than those formed by conventional milling. This is evidenced by the XRD patterns after EDAMM that show sharp peaks indicative of larger crystal sizes, as compared to the diffuse peaks observed by Balaz et al. after conventional milling [3].

5. Conclusions

PbS and Sb_2S_3 have been successfully reduced with both Fe and Mg using the novel synthesis technique of electrical discharge assisted ball milling. This is the first ever report of the reduction of PbS and Sb_2S_3 using Mg as the reducing agent. In addition, EDAMM has been shown to be the fastest synthesis route for the reduction of these sulfides with Fe, requiring only one quarter of the time compared to conventional ball milling.

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